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Radical polymerisation process and additives for synthetic resins so prepared.

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Abstract of EP0035729 (A2)

A process for the free-radical polymerisation of acrylic acid and methacrylic acid, esters and amides thereof, acrylonitrile and styrene using a liquid medium which is a melt of organic compounds which are solid at room temperature, preferably saturated or unsaturated, straight-chain or branched fatty acids having up to 30 (from 8 to 28) carbon atoms, or derivatives thereof (esters, amides or fatty alcohols) having drip points of between 25 and 120 DEG C (40 to 110 DEG C). The ratio by weight between the monomers and the solid organic compounds is from 10 to 90/90 to 10 (25 to 75/75 to 25). The process allows the direct preparation of plastics additives for plastics processing, specifically for the processing of elastomeric, thermoplastic polymers, and thermosets, in particular by thermofforming.

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Description EP0035729

[0001] The present invention relates to a process for free radical polymerization of unsaturated monomers using inert solvents, such as reaction medium.
The new process allows the production of polymer-containing compositions which can be further processed for many purposes without removal of the polymerization.
In particular, the invention relates to a process for free radical polymerization of acryls and methacrylic acids, their derivatives, and vinyl.
The knowledge gained by the novel method polymer-containing compounds are highly effective additive systems for the plastic processing, especially for the processing of polyvinyl chloride.

[0002] In the bulk polymerization of the monomers are polymerized without dilution medium and go through the viscous liquid from the solid state.
The need for all polymerizations heat of reaction is high, especially for very reactive monomers such as methyl acrylate, acrylic acid or ethylene tetrafluoromethylene a difficult problem to solve due.
Moreover, the obtained polymer can be removed only with difficulty because of their high viscosity of the reaction vessel and processes.

[0003] In solution, the monomers, dissolved in the solvents used, the resulting polymers can be soluble or insoluble.
The solvents used in the practice of water or low molecular weight organic solvents such as aliphatic or aromatic hydrocarbons, esters, ethers, alcohols and ketones.
The viscosity of the reaction mass in the solution is much lower than in the case of bulk polymerization, however, requires a considerable amount of additional costs not only for facilities for the removal of the solvent from the polymer, but also for the recovery and purification of the solvents.
Polymers are usually produced by this method only if the solutions are used as such, for example, paints and adhesives, the polymers in the liquid thus means that in the dissolved state goes used.

[0004] The present invention was to find liquid polymerization media, which are liquid at normal polymerization temperatures, but not at room temperature or at the temperature of processing (powder or waxy solids), and so further processing of the polymer as a solid mass, while avoiding a separation operation permit from the usual liquid polymerization medium.
Another specific object of the present invention was to find such a polymerization media, the finding for the synthesis of polymeric additives for the plastic processing as a flow promoter or release agent or other plastic additives on acrylic and methacrylic esters and ethylene-based, with the added at room temperature polymerization an inert material with no negative effects or even a second active component for the further process of the plastic processing represents.

[0005] According to the invention this object is achieved by a process of free-radical polymerization of unsaturated monomers using inert solvent, which is characterized in that the polymerization is carried out in the melt of solid organic compounds at room temperature.
Preferably, the polymerization at room temperature, solid fatty acids or their derivatives with dropping points 25-120 [deg].
C, particularly between 40 and 110 [deg].
C performed (see "Ann. scope, paints" (1954), p. 1008).
Those responsible for the polymerization of suitable fatty acids are solid at room temperature, in particular up to 30 carbon atoms in the molecule.
This is also true for their derivatives such as esters, amides and / or fatty alcohols.

[0006] A particularly preferred group are saturated or unsaturated, linear or branched fatty acids with 8 to 28 carbon atoms in the molecule and / or derived therefrom ester and / or partial ester of mono- to hexafunctional aliphatic or cycloaliphatic alcohols and / or fatty and amides, where the nitrogen may be substituted with 1 to 2 alkyl groups with up to 15 carbon atoms.
Optionally, the alkyl radicals are also part of the nitrogen as a ring.

[0007] The fatty acids are suitable for the process at a chain length of up to 30 carbon atoms, but preferably contain 8 to 28 carbon atoms in the molecule.
They can form double bonds can be saturated and linear and branched.
It is also possible that the fatty acids are substituted with one or two hydroxyl groups or some chlorine atoms.
However, the number of chlorine atoms does not exceed the number 6.
Suitable fatty acids can be produced from natural materials or synthesized in known way.
Also suitable are the so-called monoamides, where have eight to twenty chains up to 30 carbon atoms, in addition to the fatty acids themselves suitable are the esters or partial esters of mono-aliphatic or cycloaliphatic alcohols to hexafunctional.
Suitable alcohols with the mono alcohols up to 18 carbon atoms, especially methanol, ethanol, propanol and butanol.
Among the polyhydric alcohols are the ethanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol or mannitol.
Unless there are derivatives of fatty acids with polyhydric alcohols, the hydroxyl groups can be only partially esterified.
Suitable cycloaliphatic alcohols for example, the cyclohexanol or 1,4-cyclohexanediol.

[0008] The inventive method suitable for the amides derived from those projected, characterized from fatty acids.
Here, the nitrogen with 1 to 2 alkyl groups may be substituted.
Substituents on the nitrogen out of the group methyl, ethyl, propyl, butyl and cycyl.
If the radicals are joined to form a ring, the ring 5, and 6 is preferred.

[0098] According to another preferred embodiment, the inventive polymerization in aliphatic natural or synthetic, optionally double bond containing mono-alcohols, with 8 to 20, more preferably 8 to 18 carbon atoms in the molecule.

Fatty sulfates are esters of mono- and di-carboxylic acids.

The above mentioned mono-alcohols may have from 1 to 2 double bonds and are characterized by reduction of the corresponding fatty acid alkyl esters, particularly fatty acid methyl esters are readily available.

As emulsifying agent alongside short-chain mono-carboxylic acids such as acetic acid or propionic acid is quaternary dihydroxy- acids such as adipic acid, sebacic acid and terephthalic acid.

[0099] If the emulsifier are met in accordance with the dropping point, numerous derivatives of fatty acids and fatty acid itself suitable.

An overview of such compounds is found in the journal "Plastics, Plastics," 2 (1975), p. 17 ff and in the magazine "Plastik" 66 (1976), p. 697.

[0100] Suitable monomers for the method of the invention are suitable, methylallyl unsaturated such types such as acrylyl acid, methacrylic acid and their esters, acrylonitrile, vinyl acrylamide, or styrene. The following may be mentioned here: acrylyl acid, methyl acrylate, ethyl acrylate, polyacrylate, acrylic acid 2-ethyl hexyl acrylate, allyl methacrylate, butyl methacrylate and the esters of butanediol, ethylene glycol or tetrahydrofuran with acrylic acid or methacrylic acid.

Furthermore, the di- and tri-carboxylic acids, acrylonitrile, acrylamide, which may be substituted on the nitrogen, such as the Methylvinylpyrrolidone or crotonylacrylamide or the tert-butyl acrylamide.

Other suitable monomers such as isobutyl-methyl styrene, p-chloro styrene or methyl styrene, divinylbenzene, dicyclopentadiene and isoprene as well as

[0101] Preferred monomers or monomer mixtures, polymers or copolymers which are effective additives for the process processing, specifically for the thermoplastic processing of polyvinyl chloride, it is for methyl methacrylate, methyl methacrylate, butyl acrylate, and mixtures of stylyl acrylate, methyl methacrylate also mixtures of acrylic acid, butyl methacrylate and styrene may relationship. For example, for the production of a so-called flow copolymers and ethyl acrylate, a copolymer of methyl methacrylate suitable. A polymer of butyl acrylate or also suitable as release agents in the processing of polyvinyl chloride, when certain known proportions are maintained.

[0102] The inventive method used by the inert diluent of the polymerization temperatures have relatively low to medium viscosity maximum.

They are so easy to use liquids.

Therefore, the removal of polymerization is relatively easy and even greater approaches can be well carried out.

The weight ratio of monomers to the solid at room temperature inert diluent should be between 10 : 25 and 40 : 100, particularly 25 : 75 and 75.

Practically, it is determined by the desired properties of the polymer-containing composition containing the final product.

[0103] Suitable initiators for the polymerization are the known conventional radical initiators such as peroxides, for example, dicumyl peroxide, benzoyl peroxide or hydroperoxides such as cumene hydroperoxide. However, also compounds are preferred as azobisisobutyronitrile.

The polymerization is carried out so that the appropriate solid inert diluent are prevented and melted.

Usually you can in the monomer or monomer polymerization initiator distributed run slowly.

We choose such an initial temperature, the polymerization starts rapidly.

In total polymerization, the reaction generally after 2 to 6 hours is completed.

[0104] Of course it is also möglich to carry out the polymerization continuously, for example, the first part in a reaction tube, where it feeds the liquefied inert diluent simultaneously with the monomers to be polymerized.

Here, the initiator at once or at different locations may be added.

After performing the first reaction step, then a secondary reaction in a collecting vessel is possible.

[0105] In the case of acrylyl acid and methacrylic acid esters of lower alcohols such as ethyl acrylate and methyl methacrylate or in the case of polymerization of styrene, the polymerizations run as a dispersion or precipitation polymerization.

The monomers are soluble in the melt of the fatty alcohol and fatty derivatives, the polymers are insoluble.

Depending on the reaction you get more or less finely divided polymer precipitation or finely divided suspensions with particle sizes between 0.1 μ m up to 3 μ m.

[0106] The copolymerization of such monomers, which form soluble and insoluble polymers, for example, in the copolymerization of methyl methacrylate and butyl methacrylate, go through the solid phase polymerization, which can lead to uncontrolled clogging.

In these cases, the concentration use of 0.1 to 15 weight percent, based on monomer, a special emulsifier prevent autoemulsion, since it effectively prevents both the liquidation and the particle size influenced. Such emulsifiers for non-aqueous systems, such as polymers or graft copolymers of methyl methacrylate with butyl methacrylate or ethylhexyl acrylate or prop-2-methylacrylate itself and its copolymers with other acrylyl and methacrylic monomers.

An overview of suitable emulsifiers are, for example, Encyclopedia of Polymer Science and Technology Interscience Publishers, New York, "Non-aqueous dispersions."

[0107] prepared by the method of the invention are polymers in the molecular weight ranges from about 500 to 5,000,000, in particular 1,000,000 to 1,000,000,000, whereas the polymerization is usually events a weak terpolymerization.

By further use of typical fillers such as aliphatic hydrocarbons and the molecular weights - such as from other known polymerization processes - reduce.

The concomitant use of di- and multi-functional monomers such as divinylbenzene, dicyclopentadiene or increase the molecular weights up to the formation of insoluble gels.

[0108] The resulting polymer-containing compositions are enclosed, depending on the type of polymers and the fatty alcohol and fatty acid derivatives and depending on the weight ratio of both components contained very solid to powdery products.

The workup of the melting or melting is more advantageously cooled by spray cooling from the processing or other heavy fatty acid derivatives of known methods.

In many cases, you can grind the polymer-containing composition at room temperature or under refrigeration if necessary to fine powder.

[0109] The results obtained in the inventive process - reaction products are valuable synthetic additives that can be used for processing of thermoplastic and thermosetting polymers are used under not deformation.

In particular, the invention according to available plastic additives for thermoplastic processing of polyvinyl chloride or copolymers of vinyl chloride are suitable.

Apart from this main use they can of course also in the processing of thermoplastic polymers used by others, if proper conditions are met.

These are given under certain circumstances in the processing of polypropylene, polyethylene, copolymers of ethylene with vinyl acetate, polymethacrylates, copolymers of methyl methacrylate with other monomers, polyurethanes, polyamides and particularly linear polyesters.

Examples

The polymers

[0021] In a 2-l-Plasticizerchamber glass with stirrer, thermometer and dropping funnel were placed at room temperature and solid hal derivatives by heating to 20 to 120 [deg.] C. liquefies.

In the course of 2 to 6 hours digested the monomer and the polymerization initiator to be evenly and allowed to rest for 20 minutes to complete the conversion.

In some cases, is added to the reaction polymeric emulsifiers or protective colloids to obtain finely divided polymer emulsions or suspensions to.

The copolymer-containing composition was converted by grinding on sheet.

[0022] In the following table are given after the serial number of the example, the reaction medium, the monomer, the initiator (AIBN = azobisisobutyronitrile, CA = decyl).

As an emulsifier was always poly-2-acrylate of acrylates is used, if one proved necessary.

This is followed by polymerization temperature and duration.

This gave a solid homogeneous solutions or fine dispersions.

[0023]

Application of the products

[0024] The products produced by the above examples were good lubricant or release agent.

The product of Example 6 and 8 was a so-called "flow-promoter" used, meaning that it conveyed an inner sliding in the processing of PVC and thus reduced the plasticizing.

[0025] The product of Example 4 was examined in more detail on his release and lubricating properties. The experiments were performed on a laboratory rolling mill as a roll Benson® dimensions of 450 x 220 mm.

a) The following approach has been made:

On the rolling mill were made runs and the time up to stick to the roll.

When using the comparison mixture was fast-free time of 1 minute, with the inventive product used in Example 4 38 minutes.

Then the experiment had to be canceled because the thermal stability of the strip was limited.

The experiments were [deg.] At a roll temperature of 500

C made.

b) A basic approach has been established:

The experiment was [deg.] At a roll temperature of 185

C made.

The comparison as a lubricant mixture contained 1 part by weight of glycerol mono oleate, 0.5 parts by weight of fatty acid esters of octylphenol, 1 part by weight of a copolymer of methyl methacrylate and ethyl acrylate.

Was used for comparison in a second trial, the product of Example 4 in the same amount.

It was the pressure in the nip measured at different speeds and get the following results:

c) The product of Example 7 was carried out following comparison test.

[0026] In one Plasticorder Extruder was the mixture at 165 °C and examined at 30 rpm.

It has been compared as a lubricant used 2 parts by weight of phthalic acid di-ester of a C16/18-

Fattyalcohol and 1 part by weight of a commercially available copolymer of methyl methacrylate and ethyl acrylate.

[0027] In contrast, three were then threaded sole parts used in Example 7 of the manufactured product.

It was proven that the used sample with the product as desired non-plasticized, because the sliding action was very high.

Under the same conditions, the comparison sample was plasticized after 2.7 minutes.



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Claims EP0035729

First

Process for free radical polymerization of unsaturated monomers using inert solvent, wherein the polymerization is carried out in the melt of solid organic compounds at room temperature

Second

The method of claim 1, wherein the polymerization at room temperature, solid fatty acids or their derivatives with dropping points 25-120 [deg.] C, particularly between 40 and 110 [deg.] C is performed

Third

Method according to obtain 1 or 2, wherein the polymerization is carried out in the melt of fatty acids are solid at room temperature for up to 30 carbon atoms and / or their derivatives such as esters, amides and / or fatty acids

4th

Method according to claims 1 to 3, characterized in that the polymerization in the saturated or unsaturated, linear or branched fatty acids with 6 to 28 carbon atoms in the molecule and / or derived therefrom esters and / or partial esters of mono- to hexafunctional aliphatic or cycloaliphatic alcohols and / or fatty acid amides, the nitrogen with 1 to 2 alkyl groups with up to a total of 16 C-atom be substituted carbon atoms, is made.